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(54) Titre : UTILISATION D'UN NYLON-12 POUR LE FRITTAGE SELECTIF AU LASER
(54) Title: USE OF A NYLON-12 FOR SELECTIVE LASER SINTERING

(57) Abrégé/Abstract:
Disclosed is a process for producing shaped articles by selective laser sintering of pulverulent material of nylon-12 having a melting point of 185 - 189°C, an enthalpy of fusion of 112 ± 17 J/g, and a solidification point of 138 - 143°C. The pulverulent nylon-12 preferably has a mean particles size of from 50 to 150 µm.

ABSTRACT OF THE DISCLOSURE

Disclosed is a process for producing shaped articles by selective laser sintering of pulverulent material of nylon-12 having a melting point of 185 - 189°C, an enthalpy of fusion of 112 ± 17 J/g, and a solidification point of 138 - 143°C. The pulverulent nylon-12 preferably has a mean particles size of from 50 to 150 μm.

Use of a nylon-12 for selective laser sintering

The invention relates to a process for producing shaped articles by selective laser sintering of pulverulent materials, in which a nylon-12 (polylaurolactam; PA 12) having certain physical characteristics is used as pulverulent material.

In the development of machinery and apparatus, the production of samples, models and prototypes plays an important part and has an influence on the development time. The production of such shaped articles is, however, time-consuming in its own right and therefore likewise influences the development time. In recent times, a process has become known which is termed selective laser sintering (or rapid prototyping) and which permits rapid and low-cost manufacture of such shaped articles from a pulverulent material, generally from a polymer powder. The process follows on from computer-aided design (CAD), which gives sectioned images of the desired shaped article in digitalized form.

For producing the shaped article, the polymer powder is applied in a thin layer onto a table, capable of being moved downward, in a sintering chamber which has been heated to a temperature slightly below the melting point of the polymer. The layer thickness is selected so that a melt layer is produced after the subsequent laser sintering. The laser sinters the powder particles together as instructed by the computer. After this, the table is lowered by an amount corresponding to the layer thickness, usually from 0.2 to 2 mm. The procedure is repeated by applying a fresh layer of powder. After the pre-selected number of cycles has been completed, a block has been produced with the intended number of layers and consisting on the outside of powder, hiding an interior consisting of a highly viscous melt in the shape of the desired shaped article. Unmelted regions, in which the powder is still present in solid form, stabilize the shape of the melt.

The block, consisting of powder shell and melt, is then slowly cooled, and the melt solidifies as the temperature goes below the solidification point of the polymer. It is advantageous here if the block is held at the solidification point until the phase change is completed. This is achieved by selecting a low cooling rate in the temperature range of the phase change, so that the liberated heat of solidification holds the shaped article precisely at the solidification point in the interior of the block until the phase change is completed. After cooling, the block is removed from the sintering chamber, and the shaped article is separated from the unsintered polymer powder. The powder can be reused for the process.

The requirements for maximum suitability of a polymer for laser sintering are:

- a very high difference between melting point and solidification point. Since in pure polymer powders the solidification point is determined by basic physical data, increase of the melting point by forming a new crystal modification implies a great advantage. The larger the difference, the smaller is the shrinkage on solidification and the more precise is the achievement of the desired dimensions of the shaped article. A lowering of the solidification point by means of additives or comonomers generally has an adverse effect on the mechanical properties.

- a very high enthalpy of fusion. This prevents powder particles located in the neighborhood of the particles affected by the laser beam from beginning to melt as a result of unavoidable conduction of heat, resulting in a sintering taking place outside the desired area.

The pulverulent polymer most frequently used is nylon-11 (PA 11); other polymers used as nylon-6, polyacetals, polypropylene, polyethylene and ionomers. Polycarbonates and polystyrene have also been used. The suitability of the polymer powders is a function of physical characteristics as well as their chemical nature. WO 96/06881 describes a polymer powder which is suitable for laser sintering and which, when its melting behavior is determined by differential scanning calorimetry (DSC) at a scanning rate of 10-20°C/min, shows no overlapping of the melting peak and the solidification peak and which has a degree of crystallinity of from 10 to 90%, also determined by DSC, a number-average molecular weight Mn of from 30,000 to 500,000 and a ratio Mw/Mn in the range from 1 to 5. According to WO 96/06881, this powder is used together with a reinforcing powder whose melting point is considerably higher than that of the polymer, for example glass powder.

It has now been found that shaped articles can be produced in an advantageous manner by selective laser sintering of pulverulent material if nylon-12 having the following characteristics is used as pulverulent material:

Melting point	185 - 189°C
Enthalpy of fusion	112 ± 17 J/g
Solidification point	138 - 143°C.

A preferred nylon-12 has the following characteristics:

Melting point	186 - 188°C
Enthalpy of fusion	100 - 125 J/g

Solidification point 140 - 142°C.

The various characteristics were determined by means of DSC according to DIN 53765 and AN-SAA 0663. The measurements were carried out using a Perkin Elmer* DSC 7, with nitrogen as gas for flushing and a heating rate and cooling rate of, respectively, 20 K/min. The temperature measurement range was from -30 to 210°C.

The use of the specific PA 12 powder according to the invention for the laser sintering is associated with advantages which powders of the prior art do not have, or have to only a small extent. Surprisingly, this applies both to the conventional PA 12 and to the PA 11 widely used as powder for selective

* Trade-mark

laser sintering. For these polyamides ~~and also for PA 12 grades according to~~ the invention, the following data relevant for laser sintering were measured:

Polyamide	Melting point	Enthalpy of fusion	Solidification point
PA 12[1]	187 ± 1°C	112 ± 17 J/g	141 ± 1°C
PA 12[2]	177 ± 1°C	71 ± 11 J/g	141 ± 1°C
PA 12[3]	176 ± 1°C	109 ± 16 J/g	143 ± 1°C
PA 11[4]	186 ± 1°C	87 ± 13 J/g	157 ± 1°C

1 PA 12 according to the invention

2 VESTAMID(R) from Hüls AG (polymerized hydrolytically)

3 ORGASOL(R) from Elf Atochem S.A. (polymerized in solution)

4 RILSAN(R) from Elf Atochem S.A. (polymerized hydrolytically)

The table shows that the PA 12 according to the invention shows the most favorable combination of (largest possible) difference between melting and solidification points and also (largest possible) enthalpy of fusion. This means that the temperature in the sintering chamber can be held at a higher level than is the case with commercially available polyamides. The result is that the shrinkage on solidification (curl) is lower and the dimensional stability of the shaped articles is higher than when these other polyamides are used.

Shaped articles made from the powder used according to the invention have such a good surface that they do not require post-treatment for many applications. In addition, the dimensional stability of the shaped articles is better than that of shaped articles made from other polyamides. The relatively steep melting peak allows the temperature in the form to be held without difficulty at just below the melting point. This means that there is no need to introduce excessive amounts of energy via the laser and, even under these conditions, there is no likelihood of caking of particles in the zones not covered by the laser beam. The powder in these zones is therefore better suited for reuse than conventional PA 12 or PA 11 powder. Because its

melting point is higher, the liquid product after melting of tho PA 12 powder to be used according to the invention is markedly less viscous than a melt of conventional PA 12 at a temperature exceeding its melting point by the same extent. The shaped articles have relatively few pores, evidenced by the fact that their density is only slightly below the density of shaped articles produced conventionally (i.e. by injection molding, extruding, etc.). The strength of the shaped articles is correspondingly high. PA 12 is very tough, and the shaped articles can therefore be subjected to high stresses. The water absorption of PA 12 is moreover very low, and the shaped articles do not therefore tend to swell when in contact with water.

The PA 12 powder used in the process of the invention is known per se and is expediently prepared by the process of DE 29 06 647 B1, by dissolving PA 12 in ethanol and allowing it to crystallize out under particular conditions, giving a powder having particle sizes in the µm range.

The process according to the invention has no special features with regard to the other properties of the PA 12 material or the process conditions for the selective laser sintering. The mean particle size and the particle size distribution determine, inter alia, the surface area tolerances, which are always larger than the mean particle diameter. The PA 12 powders generally have mean particle sizes of from 50 to 150 µm. If desired, the particles of the PA 12 obtained as described above are further comminuted by grinding and graded to meet requirements.

The characteristics of the process, such as layer thickness, temperature in the form, strength of the laser radiation, distance of the layer from the radiation source, irradiation time and cycle frequency, may easily be determined for a given shaped article by exploratory experiments.

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CLAIMS:

1. A process for producing a shaped article, which comprises selective laser sintering of a pulverulent material of nylon-12 having a melting point of 185 - 189°C, an enthalpy of fusion of 112 ± 17 J/g and a solidification point of 138 - 143°C.

2. A process as claimed in claim 1, wherein the nylon-12 has a melting point of 186 - 188°C, an enthalpy of fusion of 100 - 125 J/g and a solidification point of 140 - 142°C.

3. A process as claimed in claim 1 or 2, wherein the nylon-12 pulverulent material has a mean particle size of 50 to 150 μm.

4. A process as claimed in any one of claims 1 to 3, which comprises:

(a) applying the pulverulent material in a thin layer onto a table capable of being moved downward in a sintering chamber which has been heated to a temperature slightly below the melting point of the pulverulent material, wherein the thin layer has such a thickness that a melt layer is provided after a subsequent laser sintering;

(b) applying laser to sinter particles of the pulverulent material of the thin layer in a sectioned image form according to a computer-aided design (CAD);

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(c) lowering the table by an amount corresponding to the thin layer thickness;

(d) repeating the steps (a), (b) and (c) a preselected number of cycles until a block has been produced with an intended number of layers and consisting of the pulverulent material on the outside and a highly viscous melt as an interior; and

(e) slowly cooling the block to allow the melt to solidify.

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PATENT AGENTS